

# Atmospheric pressure gliding arc with side inlet applied to polypropylene treatment and deposition of thin plasma polymer layers

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**Abstract:** Polypropylene (PP) strips were modified by a gliding arc jet with side inlet allowing the injection of gas additives or monomers (hexamethyldisiloxane, n-hexane) into the non-thermal region of plasma. The wettability and adhesion of the PP used in PP-epoxy adhesive-alumina bonds increased after all treatments. Homogeneity of the treatment increased while Ar was injected into dry air by the side inlet. Aging of the treatment assessed by the contact angle measurements with water and diiodomethane was influenced the measurement itself.

**Keywords:** polypropylene, gliding arc, adhesion, plasma treatment, plasma polymer

## 1. Introduction

Polypropylene (PP) is a cheap, fully recyclable synthetic polymer [1]. Due to its useful properties, such as high chemical resistivity or good electrical isolation, the PP applications range from automotive industry [2] to food packaging [3]. However, the surface energy of PP is low,  $27 \text{ mJ}\cdot\text{m}^{-2}$ , and for many applications its surface modification is required.

Atmospheric pressure plasma discharges offer fast, environmentally friendly alternative to the standard surface chemical treatment by toxic primers. Among the many different non-thermal plasma sources (corona, dielectric barrier discharge etc.), atmospheric pressure gliding arc is unique for its hybrid thermalization character. It is ignited between electrodes as the thermal arc discharge which evolves into the non-thermal plasma when being pushed away from electrodes by gas flow [4]. The combination of the equilibrium and non-equilibrium plasma together with the high efficiency of vibrational excitation paths leads to a high concentration of reactive species needed for the quick and efficient plasma treatment [5].

Usage of dry or humid air is preferable in industrial applications. Therefore, mixing gas additives into the discharge to further improve its efficiency should be considered. Nonetheless, in all published studies [6, 7], additives were mixed into air before the plasma ignition leading to their unwanted fragmentation in the thermal plasma region.

In this work, we present a novel approach to the surface modification of polypropylene utilizing an industrial gliding arc running in dry air and with gas additives being injected into its non-thermal region by a side inlet.

## 2. Experimental details

The samples treated by the gliding arc were polypropylene sheets with the thickness of 5 mm (Omniplast) produced by the extrusion of a PP granulate using three rollers. The experiments were carried out on the less rough side after removal of the protective foil and cleaning the glue residues by wiping the surface with isopropanol (IPA) and cyclohexane-soaked cleanroom wipes and 10 minutes ultrasonic bath in IPA.

Industrial gliding arc jet GVN1k-2011 (Surface Treat) operating at the driving voltage 230 V with frequency 50 Hz was used for the surface treatment. The power was set to 450 W. The compressed dry air with the flow rate 11.8 slm was used as the discharge working gas. A conveyor belt with a set constant speed 100 mm/s (22 mm/s for some of the depositions) was used to move the treated samples. Two passes with the offset of 5 mm from the sample axis, i.e. with the relative vertical shift of 10 mm, were applied.

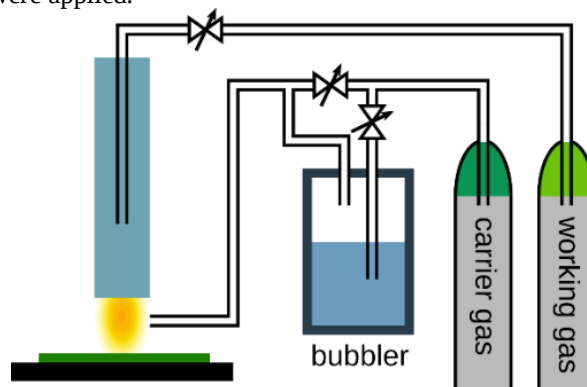


Fig. 1. Scheme of the gliding arc jet set-up with the side gas injection system.

Vapors of volatile gas compounds (ethanol, IPA), water and monomers (HMDSO, n-hexane) were added to the gliding arc. For water, ethanol and IPA vapors the constant flow of 15 sccm was used. For monomers the flow rate was set higher, ranging from 24 to 71 sccm for HMDSO and 159 to 317 sccm for n-hexane, to ensure deposition of a thin layer. Vapors were transported to the non-thermal plasma region of the gliding arc jet using two argon lines as in Fig. 1. The first line passed through the bubbler where the argon was used to collect vapors of the used liquid. The flow rate in this line was set by M-Series Alicat Mass flowmeter according to the bubbler equation [8]. The second line with another Alicat Mass flowmeter was used to keep the overall argon flow constant. The correct value of the overall argon flow at which the additives reach active plasma region was determined by numerical simulations of the gas flow dynamic as 1.5 slm.

The polypropylene surfaces were characterized by contact angle measurements, X-ray photoelectron spectroscopy (XPS) and nanoindentation measurements. The adhesion between the PP and aluminum stripes bonded together by epoxy adhesive DP 190 (3M) was evaluated by the tensile tester. Optical emission spectroscopy (OES) and ultrafast camera photography were used for plasma diagnostics of the gliding arc jet.

### 3. Results and Discussion

The elemental analysis done by XPS revealed the presence of functional groups containing oxygen and nitrogen after the treatment of the PP surface in the gliding arc jet working in either dry air or a mixture of dry air, Ar and a vapor additive. The highest concentration of O and N (Fig. 2) was observed for the PP treated in the dry air/Ar mixture which we attribute to presence of Ar\* metastables prolonging life time of active plasma species such as OH group. As a result, the volume of observed filaments increased, and the treatment became more homogeneous.

Addition of water and organic volatile compound vapors into the discharge did not change, in the range of expected experimental errors, the atomic concentrations of elements. However, the water contact angles (WCA; Fig. 3) which are sensitive to the concentration of functionalities at the uppermost layer of the surface decreased. The discrepancy between these two measurements might be explained by formation of a ultrathin plasma polymer layer that did not contribute significantly to the chemical composition determined by XPS with the penetration depth 3–5 nm and/or by different surface roughness.

Tensile strength of the PP-epoxy-Al bond increase after all treatments circa 6 times and can be well correlated with the atomic concentration results. We would like to highlight that the decrease of the WCA caused by plasma treatment did not lead to an increase of the tensile strength of the bonding as often cited in literature [9].

Nanoindentation test revealed the increase of the surface indentation hardness after the plasma treatment.

These results could be explained by a higher cross-linking degree promoted by UV radiation from plasma (observed by OES) and local melting of the PP caused by direct interaction of plasma filaments with the surface that was observed by ultrafast camera. The rotational temperature calculated from OH radicals was as high as  $4160 \pm 70$  K.

Intermixing of the n-hexane vapors with air in the plasma region resulted in the deposition of plasma polymer layers contained up to 32 at.% of O and 7 at.% of N. All the WCAs were lower than  $40^\circ$ . For all the tested conditions the tensile strength was  $\sim 8$  MPa which is slightly lower than in the case of the plasma treatment in dry air or a mixture of dry air/Ar.

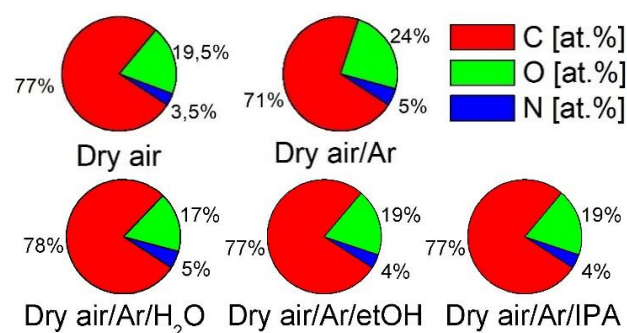


Fig. 2. Atomic composition (without H) of the polypropylene surface after treatments at 100 mm/s. Presence of only C was detected in the reference untreated sample.

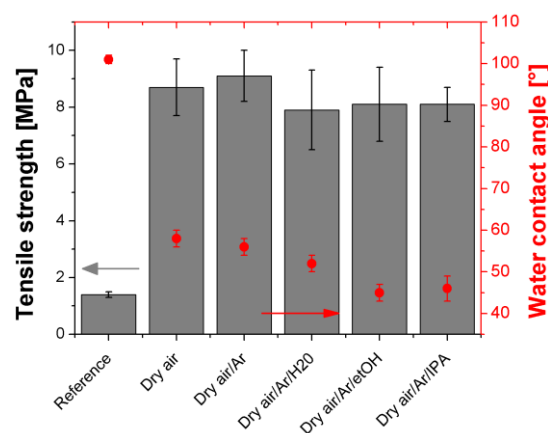


Fig. 3. Correlation of the tensile strength and WCA results for treatment speed 100 mm/s.

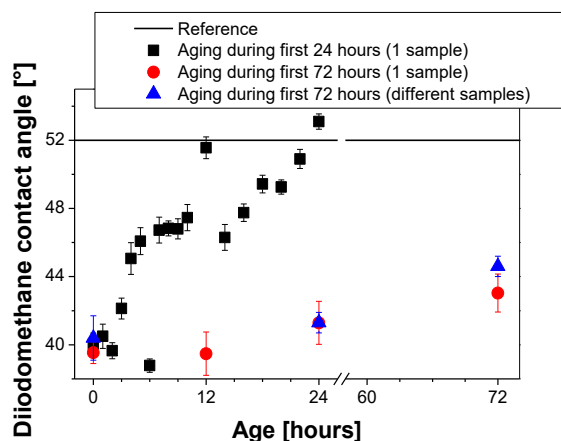


Fig. 4. Influence of the time intervals between the measurements on the diiodomethane contact angles for the samples modified in dry air and the movement speed 100 mm/s.

HMDSO thin layers were composed from O (up to 57 at.%), Si (up to 36 at.%) and C. Nitrogen was not observed which is in good correlation with the assumption that the fragmentation of the HMDSO molecules is caused by the reaction of oxygen atoms and/or molecules with the HMDSO organic moieties [10]. Deconvolution of the high-resolution Si peak lead to the identification of a  $\text{SiO}_x$  inorganic character of deposited polymers. As  $\text{SiO}_x$  functional groups has high hydrophilicity, the WCAs were low (the lowest value was  $12^\circ$ ). However, the good hydrophilicity and high free surface energy did not lead to the highest tensile strengths of the PP-epoxy-Al bond that increased only 3 times (tensile strength  $\sim 5$  MPa).

As the plasma treatment is known for its fast aging, we looked at the time dependence of the contact angles and the free surface energy. We compared the results from separate samples and from different places of a single sample. If the intervals between subsequent measurements were longer, the aging of the sample was minimal (results for diiodomethane are shown in Fig. 4) probably due to the high degree of crosslinking. However, if the intervals were small ( $\sim 1$  hour) the aging of the sample was rapid. XPS analysis of the measured sample revealed a small amount of hydrophobic iodine that remained on the surface from the diiodomethane. It is also possible that static charge brought to the sample by the plastic pipette head could influence measured values. The aging of the n-hexane plasma polymer layers after 24 hours was also not observed. For the HMDSO plasma polymer the aging of WCA was rapid. The WCA increased from  $\sim 12^\circ$  to  $\sim 130^\circ$  over 24 hours. We attribute this rapid increase to the combination of chemical and structural changes.

#### 4. Conclusion

We have been able to successfully improve the PP wettability and its adhesion to epoxy-Al bond with the

gliding arc jet running either in dry air or in a mixture of dry air and a vapor additive/monomer. The XPS analyses of the treated PP and n-hexane plasma polymers revealed the presence of oxygen (17 – 30 at.%) and nitrogen (3 – 7 at.%) containing functional groups that lead to the decrease of WCAs (from  $101^\circ$  to  $56^\circ$  and lower). The thin layers deposited from HMDSO monomer had an inorganic  $\text{SiO}_x$  character. The tensile strength of the PP-Al-bond ranged from 5 to 9 MPa. In addition to the modification of the chemical composition of the PP surface, the plasma exposure lead to the increase of the degree of crosslinking which in turn lead to slower aging process. However, we were able to influence the aging speed by changing the interval between the subsequent measurements. The quick intervals between measurements lead to faster aging of the PP.

#### 5. Acknowledgement

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